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A comparative study on the morphological features of highly ordered titania nanotube arrays prepared via galvanostatic and potentiostatic modes

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ABSTRACT

The formation of highly ordered, vertically aligned titania (TiO_2) nanotubes (NTs) via the cost effective galvanostatic and potentiostatic anodization techniques is reported. In both the approaches, the variation of water content in terms of fresh and used ethylene glycol based electrolyte has been considered as a significant parameter to genuinely investigate each of the anodization modes. Noteworthy differences and influences were clearly observed in terms of anodization kinetics and the resulting tubular morphology, such as architecture and arrangement during the development TiO_2 NTs arrays. The as-synthesized samples were characterized by powder X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM) and Energy dispersive X-ray analysis (EDX).

1. Introduction

Titania (TiO_2) nanotubes (NTs) have taken the research world by a whirlwind over the past decade. Interestingly, TiO_2 is the most studied material for its tubular structure among all metal oxides as its bulk counterpart is known for its biocompatibility, non-toxicity and corrosion resistance [1]. Zwilling and co-workers reported the synthesis of self organized NT arrays of titanium and its alloys through electrochemical anodization for the first time [2,3]. Subsequently, great research interest was stimulated in this field when the research groups of Grimes [4–6] and Schmuki [1,7] produced highly ordered TiO_2 NT arrays by potentiostatic anodization of Ti sheets. Since then, the research community has witnessed phenomenal growth of the TiO_2 NTs in its geometry, morphology and utility. The periodic structures with particular geometry of TiO_2 NTs have reached elevation due to their enormous applications in various fields including photocatalysis [8,9], dye sensitized photovoltaic cells [10–12], quantum dots sensitized photovoltaic cells [13,14], hydrogen generation by water photoelectrolysis [15,16], hydrogen storage [17,18], gas sensing [19,20], bio sensing [21] and drug eluting stents [22]. Each application is strongly dependent on the structural features like pore diameter, wall thickness, length, aspect-ratio and tube-to-tube spacing of the TiO_2 NTs.

Various synthesis techniques have been employed with success for the formation of TiO_2 NTs, they include sol-gel technique [23], template assisted synthesis [24] and hydrothermal process [25]. However, the potentiostatic electrochemical anodization technique [4] attracted the interest of many researchers due to its lower cost, large area fabrication, pore volume, unidirectional charge transfer and transport, and ordered arrangement [26,27]. Another factor in favor of the method is that, the TiO_2 NTs array morphology is obtained through intrinsic electrochemical self-sculpt without the need of a template. The technique follows a localized field-assisted oxidation and dissolution reactions, controlled by anodic potential, electrolyte and fluoride ion concentration. This result in producing precisely ordered nanoscale architecture by self-assembly [28]. The synthesis of TiO_2 NTs by electrochemical anodization has undergone various stages pertaining to its growth, from the formation of short (250 nm) irregular tube morphology [4] through dilute fluoride electrolytes to highly ordered longer (1000 μm) NTs arrangement by employing organic electrolytes [29]. Research in this direction has indicated that superior dimensions of the TiO_2 NTs can be attained by optimizing anodization parameters like pH, composition and concentration of the electrolyte, anodization potential, time and temperature.

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Apart from the potentiostatic and galvanostatic anodizations [30,31], several other approaches [32–40] based on electrochemical anodization had been attempted in the recent past to further improve the morphology of the TiO_2 NTs. The widespread investigation on various electrochemical methods can be ascribed to the fact that these processes are scalable, have large surface-to-volume ratio, allow precise control of the tubular geometry and pave way for patterned growth. As the properties robustly depend on the crystallinity and morphology, even diminutive variations has its value in defining the most favored application of the TiO_2 NTs produced by each of these techniques.

In this work, an attempt has been made to achieve the formation of highly ordered TiO_2 NTs using galvanostatic and potentiostatic anodization techniques. The variations in the growth rate, morphology, tube-to-tube spacing, hcp arrangement and wall thickness are analyzed on the basis of the various experimental parameters that have to be optimized. The roles of the mode of anodization and the water content level in both fresh and “used” electrolytes are investigated from the view point to achieve the growth of TiO_2 NTs with improvised architecture. Both the anodization modes are found to have good control over TiO_2 NTs morphology at lower water content. Interestingly, the growth rate was phenomenal in galvanostatic approach with fresh electrolyte at 2 and 3 vol% of water. Closer observation at higher water content indicates that both galvanostatic and potentiostatic anodization seem to have associated with disordered arrangement however, the growth rate observed to be faster with galvanostatic approach. To the best of our knowledge, the “used” EG electrolyte combination has not been studied under galvanostatic mode. Field emission scanning electron microscopy (FESEM) revealed the formation of better quality longer nanotubes even at faster rate with high quality interfaces and neat arrangement in galvanostatic approach. Further, a comprehensive evaluation of the TiO_2 NTs galvanostatically and potentiostatically produced in this work and other anodization based techniques has been made and it accentuates the better results pertaining to this work.

2. Materials and methods

2.1. Experimental

Titanium foils (97% purity, 0.127 mm thick, Sigma Aldrich) were uniformly cut into small pieces of dimension $1 \times 1.5\ cm^2$ with a selected working area of $1\ cm^2$. Prior to anodization, the foils were degreased by sonication with isopropyl alcohol, acetone and deionized (DI) water successively. Both galvanostatic and potentiostatic anodizations were performed at room temperature (approximately 26 °C) using a two electrode cell with Ti-foil as the anode and Pt gauze as the counter electrode. The back side of the Ti-foil was protected by cellophane tape to prefer one sided anodization. The distance between the vertically placed electrodes was kept as 4 cm. TiO_2 NTs formation was obtained in an electrolyte containing ethylene glycol, NH_4F (0.3 wt%) and DI water. The electrodes were vertically placed to provide better dissemination of heat formed at the bottom of the pores [34]. During the anodization process, a constant current density of $2\ mA/cm^2$ and a constant potential of 30 V was maintained for galvanostatic and potentiostatic approach respectively. The schematic representation of the experimental set-up used in this work is shown in Fig. 1. The entities were fixed based on the time taken for barrier layer formation, which took place in a comparable period of time in both the modes before the dissolution at the metal oxide-electrolyte interface took place. Three combinations of the electrolyte were prepared by making changes only in the water content with 2, 3 and 4 vol%. The experiment was performed for both fresh and used electrolytes. Used electrolyte is the solution that is already been used under same conditions and is completely ionized [41]. The above mentioned parameters were preset to understand the growth and morphology of the NTs produced through both the anodization approaches. The anodization time was constantly maintained at 5 h for all the experiments. The samples are labeled as G (galvanostatic mode)-vol% of water-A (for fresh electrolyte) or B (for used electrolyte). For example, G2A denotes galvanostatic anodization with 2 vol% of water in fresh electrolyte. Six samples were prepared and labeled as G2A, G2B, G3A, G3B, G4A and G4B. In the same manner, the samples prepared via potentiostatic (P) mode were labeled as P2A, P2B, P3A, P3B, P4A and P4B. The time dependant anodization voltage (galvanostatic mode) and current (potentiostatic mode) were recorded using a computer controlled multimeter (Keithley 2400). The anodized samples were kept overnight in the electrochemical cell and then subjected to ultrasonic cleaning in 1:1 ethanol and water solution to remove any surface debris as it peels off from the surface due to weak mechanical connection with the TiO_2 NTs layer. Subsequently, the samples were annealed at 450 °C for 5 h.

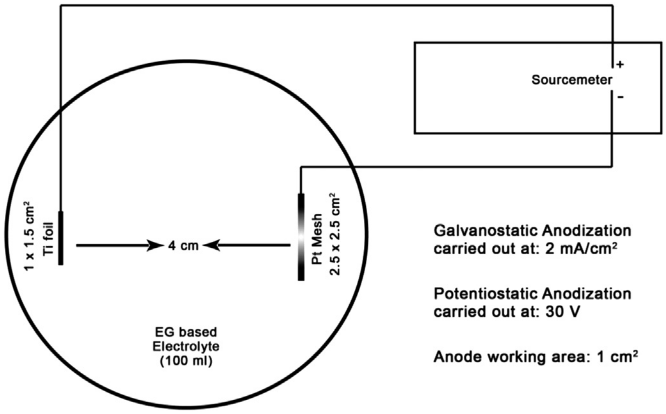

Fig. 1. Schematic diagram depicting the top view of electrochemical set-up used for galvanostatic and potentiostatic anodization.

2.2. Characterization techniques

Morphology analyses of the samples were investigated by Carl Zeiss Supra 55 Field Emission Scanning Electron Microscope (FESEM) that can be operated at various voltages from 0.5 kV to 20 kV and it is also attached with an Energy Dispersive X-ray analyzer (EDX). PANalytical X'pert pro X-ray diffractometer (XRD) with CuKα ($\lambda = 1.54060$ Å) radiation was employed to examine the crystal structure of the samples.

3. Results and discussion

The TiO_2 NTs were formed on the Ti substrate in ethylene glycol-ammonium fluoride- DI water electrolyte via galvanostatic and potentiostatic approaches, and the as-produced samples are compared. Fig. 2(a) and (b) summarizes the voltage-time (V–t) plot and current–time (I–t) plot of the galvanostatic and potentiostatic anodizations respectively. The galvanostatic anodization obviously passes through three stages of anodization. The first stage anodization behavior with a bump increase in V [Fig. 2(a)] at the initial stages of the reaction corresponds to the growth of barrier layer or compact oxide layer. Stage two is on the onset of sudden increase on the potential and it can be ascribed to the formation and pitting of the barrier layer. The gradual slow down and minimal increase in the voltage at the later stage clearly depicts the development of highly ordered TiO_2 NTs during the third stage. The V–t curves in all the reactions do not have a peak value or oscillations as reported by Taveira et al. [30] where,